

SCIENCE FOR GLASS PRODUCTION

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STRUCTURAL PARTICULARS OF IRON-CONTAINING BOROSILICATE GLASSES

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The behavior of iron in the structure of sodium iron-containing borosilicate glasses with different ratio of the glass-forming and modifying ions was studied by Mössbauer and vibrational spectroscopy. It was found that the distribution of the modifying ions differs between different types of structural species in the structure of the initial and iron-containing sodium borosilicate glasses. The addition of iron decreases the BO_4 tetrahedra fraction and increases the BO_3 triangles fraction and the fraction of the structural species Q^2 and Q^3 containing nonbridging oxygen atoms. This is accompanied by the destruction of mixed silicon borate rings and the formation of the bridging bonds Si-O-Fe^{3+} and nonbridging bonds Si-O^- , coordinated by Fe^{2+} ions.

Key words: borosilicate glass, spectroscopy, structure, iron

When iron is added to alkali borosilicate glasses, and depending on its total content and distribution between bi- and trivalent forms, a redistribution of alkali-metal ions occurs between structural positions, as a result of which the coordination state of the boron atoms and the degree of polymerization of the glass network change [1]. According to the spectroscopic data, a change in the ratio of the network-forming cations and the modifying cations in borosilicate glasses results in a change in the type and fraction of silicate and borate structural species [2 – 4], which should affect the structural and valence state of the iron. The aim of the present research is to study the behavior of iron in the structure of sodium iron-containing borosilicate glasses with different ratio of the network-forming cations and modifying cations.

METHODS OF STUDY

The compositions of the experimental glasses and their conventional designations are presented in Table 1. The glasses were synthesized from analytical grade SiO_2 , ultra-pure grade B_2O_3 , chemical grade Fe_2O_3 and chemical grade Na_2CO_3 following the procedure described in [5].

The state of iron in the structure of the glass was studied by Mössbauer spectroscopy on powder samples, using an

SM2201 spectrometer with a ^{57}Co radiation source in an Rh matrix in a constant acceleration regime in transmission geometry at room temperature. The effective thickness of the samples was 10 mg/cm^2 iron in a natural isotopic mixture, which corresponds to the thin-absorber approximation. The spectral data were analyzed using the Univem software in a two-doublet model. The results are presented in Table 2.

The structure particulars of the glasses obtained were investigated by infrared spectroscopy (IR) and Raman scattering spectroscopy (RS). The IR transmission spectra were recorded on a NEXUS Single-Beam FT-IR Spectrometer using the method of pressing the substance with KBr. An iHR 320 Labram spectrometer with an Olympus BX41 microscope was used to record the Raman scattering spectra. The spectra obtained are presented in Figs. 1 and 2.

RESULTS

Mössbauer spectroscopy of the glasses established that two forms of iron are present in the glasses — Fe^{2+} and Fe^{3+} ions. The bivalent ion fraction largely depends on the composition of the glass: as the sodium content increases and the boron content decreases in the glass the Fe^{2+} fraction decreases from 0.11 to 0.02. The isomeric shift determined in the Mössbauer spectra for bivalent iron indicates that the coordination of this iron is octahedral. This demands for the Fe^{2+} ions the role of a modifier in the glass structure and the participation of nonbridging bonds Si-O^- in the coordination

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TABLE 1. Chemical Composition of the Synthesized Glasses

Sample	Composition, molar fractions	Component content, wt. %				R^*	K^{**}
		Na ₂ O	Fe ₂ O ₃	B ₂ O ₃	SiO ₂		
15N35B	0.15Na ₂ O · 0.35B ₂ O ₃ · 0.5SiO ₂	14.6	0	38.2	47.2	0.43	1.43
25N25B	0.25Na ₂ O · 0.25B ₂ O ₃ · 0.5SiO ₂	24.6	0	27.7	47.7	1.00	2.00
35N15B	0.35Na ₂ O · 0.15B ₂ O ₃ · 0.5SiO ₂	34.9	0	16.8	48.3	2.33	3.33
F15N35B	0.9(0.15Na ₂ O · 0.35B ₂ O ₃ · 0.5SiO ₂) + 0.1Fe ₂ O ₃	11.6	20.0	30.6	37.8	0.43	1.43
F25N25B	0.9(0.25Na ₂ O · 0.25B ₂ O ₃ · 0.5SiO ₂) + 0.1Fe ₂ O ₃	19.7	20.2	22.0	38.1	1.00	2.00
F35N15B	0.9(0.35Na ₂ O · 0.15B ₂ O ₃ · 0.5SiO ₂) + 0.1Fe ₂ O ₃	27.8	20.4	13.4	38.4	2.33	3.33

* $R = \text{Na}_2\text{O}/\text{B}_2\text{O}_3$.

** $K = \text{SiO}_2/\text{B}_2\text{O}_3$.

TABLE 2. State of Iron Ions in the Structure of Iron-Containing Glasses

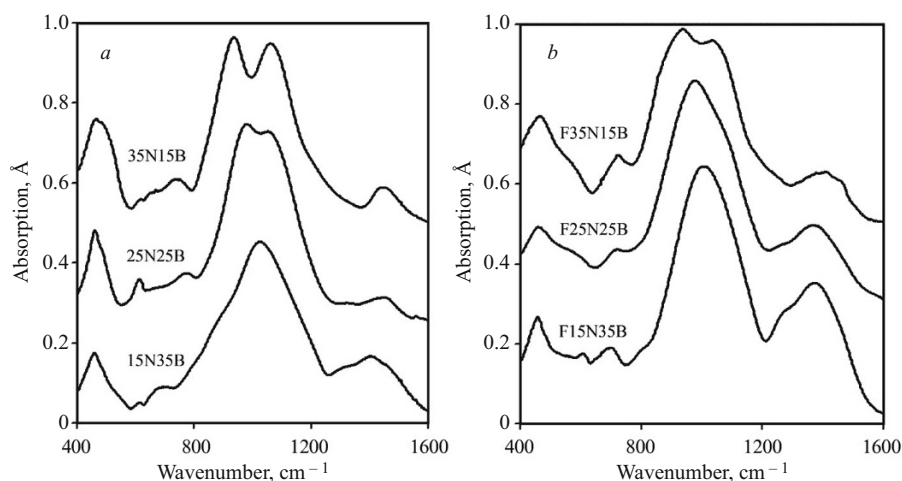
Sample	Fe ²⁺				Fe ³⁺			
	IS , mm/sec	QS , mm/sec	HW , mm/sec	$\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$	IS , mm/sec	QS , mm/sec	HW , mm/sec	$\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$
F15N35B	0.78	2.31	0.93	0.11	0.27	0.96	0.60	0.89
F25N25B	0.70	2.04	0.80	0.04	0.24	0.93	0.57	0.96
F35N15B	0.68	2.23	0.74	0.02	0.25	0.89	0.54	0.98

Notations: IS) isomeric shift relative to $\alpha\text{-Fe}$; QS) quadrupole splitting; HW) line half-width.

in the composition of the Q^n species [1, 6]. A change in the ratio $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ from 0.89 to 0.98 corresponds to trivalent iron predominating in the structure of the glass. The isomeric shift for the Fe^{3+} doublet indicates that this doublet is in tetrahedral coordination with a strongly disordered environment [6]. This demands the participation of trivalent iron in the structure of iron-containing glasses in the role of a glass-forming cation in the entire range of experimental compositions, which corresponds to the formation of the bridging bonds Si-O-Fe^{3+} in the structure of the glass.

The IR spectra for all glasses (see Fig. 1) contain bands peaking near 460–480, 710–730, 760–800, 800–1200 and 1350–1450 cm^{-1} . As the parameters R and K increase

(see Table 1) it is observed that the intensity of the band peaking at 460–480 cm^{-1} in the IR spectra of the initial glasses (see Fig. 1a) increases and that of the bands peaking at 710–730 and 1350–1450 cm^{-1} decreases. For low sodium content and high boron content (15N35B) the band in the region 800–1200 cm^{-1} , dominating in the spectrum of all initial glasses, peaks near 1030 cm^{-1} . For equal contents of boron and sodium in the glass (25N25B) this band is seen to have two distinct components peaking near 990 (low-frequency component) and 1070 cm^{-1} (high-frequency component). As the sodium fraction in the glass increases further and the boron fraction decreases the low-frequency component shifts to 945 cm^{-1} and the relative intensity of the

**Fig. 1.** IR spectra of the initial (a) and iron-containing (b) glasses.

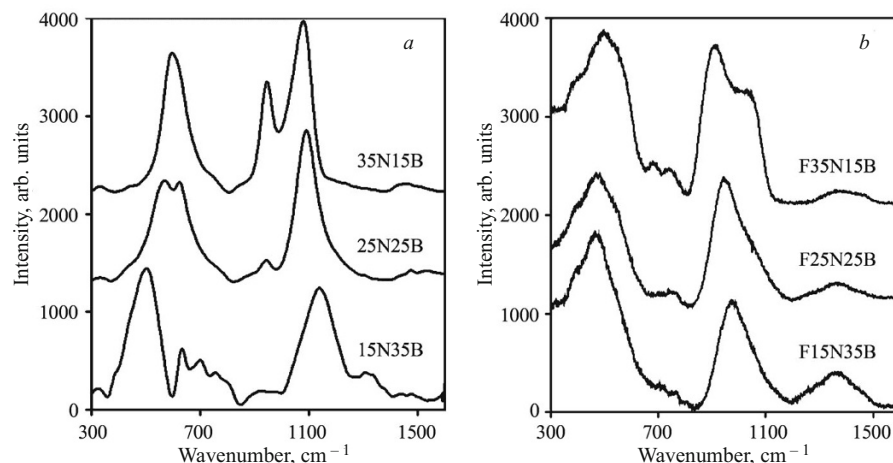


Fig. 2. RS spectra of the initial (a) and iron-containing (b) glasses.

high-frequency component increases with no appreciable change in the position of the maximum. The observed behavior of this band is explained by the fact that it is a superposition of two absorption bands peaking at $940\text{--}980$ and $1050\text{--}1090\text{ cm}^{-1}$, whose intensity changes with the composition of the glass. For all spectra (Fig. 1b) when iron is added to the experimental glasses the intensity of the band peaking at $460\text{--}480\text{ cm}^{-1}$ decreases and that of the bands peaking at $710\text{--}730$ and $1350\text{--}1450\text{ cm}^{-1}$ increases. At the same time the shape of the band dominating in the spectrum in the region $800\text{--}1200\text{ cm}^{-1}$ changes because the peak of its low-frequency component shifts in the direction of lower wavenumbers.

The IR bands in the regions $460\text{--}480$ and $1050\text{--}1090\text{ cm}^{-1}$ are due to bending and asymmetric stretching vibrations of the Si—O—Si bonds in complex silicate anions [7], and their intensity in the spectra is determined by the SiO_2 fraction in the glass. The band near $760\text{--}800\text{ cm}^{-1}$ is a manifestation of symmetric and asymmetric stretching vibrations, superposed on one another, of the Si—O⁻ and B—O—B bonds, which makes absorption in this region of the spectrum uninformative in discussions of the change in the structure of glass. The absorption in the region $940\text{--}980\text{ cm}^{-1}$ is due to bending and asymmetric stretching vibrations of the B—O bond in the BO_4 tetrahedra [8], which makes it possible to evaluate the fraction of the boron ions in tetrahedral coordination. The bands at $710\text{--}730$ and $1350\text{--}1450\text{ cm}^{-1}$ are associated with bending and stretching vibrations of the B—O bond in BO_3 triangles [7], and the change in their intensity reflects the change in the fraction of triply coordinated boron in the structure of the glasses. Analysis of the IR spectra of the initial and iron-containing glasses indicates that when iron is added to borosilicate glass the fraction due to the vibrations of the B—O bond in the BO_4 tetrahedra decreases and its fraction in BO_3 triangles increases. This is accompanied by a change in the nearest neighbor environment of the silicon atoms, which could be associated with the participation of Fe^{2+} and Fe^{3+} ions in the coordination of the charge in the nonbridging bonds of the SiO_4 tetrahedra and the formation of Si—O—Fe bridging bonds, respectively.

Strong bands peaking at 510 and 1150 cm^{-1} and a set of close weaker bands peaking at 630 , 700 and 770 cm^{-1} are present in the RS spectrum of $15\text{N}35\text{B}$ glass (see Fig. 2a). Strongly overlapping bands with peaks near 600 and 630 cm^{-1} dominate in the low-frequency range of the RS spectrum of $25\text{N}25\text{B}$ glass, and the bands in the region $700\text{--}800\text{ cm}^{-1}$ are weak. The width of the high-frequency band decreases appreciably and the peak of this band shifts to 1095 cm^{-1} in the low-frequency part of the spectrum, and a weak band appears at 955 cm^{-1} . A strong band peaking near 600 cm^{-1} and a weak band peaking near 760 cm^{-1} are present in the low-frequency region of the RS spectrum of $35\text{N}15\text{B}$ glass. In the high-frequency part of the spectrum the intensity of the 955 cm^{-1} increases significantly and the peak of the dominant band shifts to 1090 cm^{-1} .

A wide band peaking near 470 cm^{-1} with shoulders near 400 and 540 cm^{-1} dominates in the low-frequency part of the RS spectrum of $\text{F}15\text{N}35\text{B}$ iron-containing glass (Fig. 2b). Weak bands are also present at 700 and 770 cm^{-1} . The high-frequency part of the spectrum of this glass is represented by a strong band at 980 cm^{-1} and a weaker band at 1370 cm^{-1} , whose complex form is associated with the presence of shoulders near 1280 and 1450 cm^{-1} . Switching to the spectra of glasses with a higher sodium content and low boron content, the peak of the band dominating in the low-frequency part of the spectrum shifts from 470 to 485 cm^{-1} ($\text{F}25\text{N}25\text{B}$ glass) and 500 cm^{-1} ($\text{F}35\text{N}15\text{B}$ glass). This is associated with an increase in the intensity of its high-frequency shoulder near 540 cm^{-1} .

In the high-frequency part of the spectrum of $\text{F}25\text{N}25\text{B}$ glass the 980 cm^{-1} band becomes stronger owing to an increase in its shoulder peaking near 920 cm^{-1} . Two individual bands peaking near 920 and 1030 cm^{-1} are visible in this part of the spectrum of $\text{F}35\text{N}15\text{B}$ glass. At the same time going from $\text{F}15\text{N}35\text{B}$ glass to the $\text{F}25\text{N}25\text{B}$ and $\text{F}35\text{N}15\text{B}$ glasses the band peaking near 1370 cm^{-1} in the RS spectrum becomes weaker.

The bands near $400\text{--}600\text{ cm}^{-1}$ in the low-frequency part of the RS spectra of borosilicate glasses are due to symmetric stretching and bending vibrations of the bridging

bonds Si–O–Si and Si–O–B in anions with complex structure [2, 3]. The high intensity of these bonds, which is observed in the RS spectra of all the experimental glasses, indicates a relatively high degree of polymerization of their anionic structure.

The RS bands near 600 and 630 cm^{-1} reflect the vibrations of mixed silicon borate ‘rydmergite’ and ‘danburite’ rings, respectively, which are distinguished by the ratio of the silicon and boron atoms [1]. The increase in the intensity of the 600 cm^{-1} band and decrease in the intensity of the 630 cm^{-1} band with increasing parameters R and K indicate a decrease in the boron fraction in the glass as a whole and in the composition of mixed borosilicate rings. The vanishing of both bands with the addition of iron indicates the absence of mixed silicon borate rings in the structure of iron-containing glasses.

The bands in the region 700 – 800 cm^{-1} are associated with the vibrations of B–O bonds in BO_3 triangles (700 cm^{-1}) and BO_4 tetrahedra (770 cm^{-1}), but the low intensity of these bands makes it impossible to use them to determine the state of boron in the structure of the glasses.

The bands in the region 900 – 1150 cm^{-1} in the high-frequency part of the RS spectra are due to stretching vibrations of nonbridging Si–O $^-$ bonds in the structural species Q^2 and Q^3 [9]. Their presence in the spectra of the initial glasses shows that sodium ions participate in the coordination of nonbridging bonds, while the growth in the intensity and change in the position of these bands in the spectra of iron-containing glasses can be attributed to a substantial participation of iron ions in the coordination of the charge of bridging and nonbridging oxygen.

The band peaking near 1370 cm^{-1} is a manifestation of the vibrations of BO_3 structural species. The low intensity of this band in the spectra of the initial glasses indicates that boron in the tetrahedral coordination (BO_4) dominates in the structure of these glasses, while the increase in its intensity in the spectral of iron-containing glasses reflects an increase in the BO_3 fraction.

CONCLUSIONS

Mössbauer spectroscopy established the presence in iron-containing glasses of bivalent iron, in the octahedral coordination, acting as modifying cation and coordinating nonbridging Si–O $^-$ bonds in the structural species Q^n , and trivalent iron in tetrahedral coordination with a strongly disordered environment, participating in the formation of bridging bonds Si–O–Fe $^{3+}$. Analysis of the IR and RS spectra showed a difference in the distribution of modifying cations between different types of structural species in the structure of the initial and iron-containing sodium borosilicate glasses. The sodium ions in the initial glasses compensate the charge of four-fold coordinated boron and nonbridging oxygen, and their distribution between the silicate and borate parts of the structure of the glasses corresponds to the nmr data [10, 11].

In iron-containing glasses a decrease in the fraction due to BO_4 tetrahedra and an increase in the fraction due to BO_3 triangles and the structural species Q^2 and Q^3 containing nonbridging oxygen atoms are observed in the entire range of experimental compositions. This is accompanied by the destruction of mixed silicon borate rings and formation of Si–O–Fe $^{3+}$ rings and Si–O $^-$ nonbridging bonds coordinated by Fe $^{2+}$ ions.

In summary, when iron is added to sodium borosilicate glasses the interaction between boron and Na $^+$ cations becomes weaker. A significant fraction of the sodium ions in the structure of iron-containing borosilicate glasses participates in the coordination of Si–O $^-$ nonbridging bonds in the species Q^n and the charge of trivalent iron forming the Si–O–Fe $^{3+}$ bridging bonds. This corresponds to stronger bonding of Na $^+$ cations and should increase the thermal and chemical stability of matrix materials based on these glasses.

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